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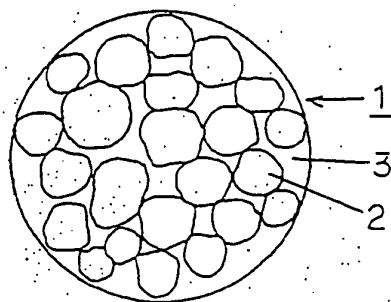
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(54) Dielectric ceramics composite material.

(57) A dielectric ceramic composite material comprising a dielectric ceramics and a glass having a softening temperature lower than the sintering temperature of the dielectric ceramics, wherein said particles of the dielectric ceramics are randomly dispersed in a matrix of the glass. This composite material can be formed by molding a mixture of the dielectric ceramics powder and glass powder at first, and by firing this mold (including a film thereof) at the softening temperature of the glass or higher. The obtained dielectric ceramics composite material can be extensively utilized as various ceramic functional elements or electronic components incorporated in various piezoelectric, pyroelectric, ferroelectric memory, actuator elements and many others.

FIG. 1



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The present invention relates to a ceramics composite material having dielectric properties. More particularly, this relates to a ferroelectric ceramics composite material to constitute piezoelectric elements applied to electric filters, oscillators, actuators and others, pyroelectric elements applied to infrared sensors and others, and ferroelectric memory elements applied to non-volatile RAMs and others. This invention
 5 relates also to an electrostrictive ceramics composite material to constitute electronics components incorporated in positioning devices of precision instruments, actuators incorporated in video tape-recorders for auto-tracking, and others.

The ferroelectric ceramics such as piezoelectric ceramics belong to the family of dielectric ceramics, and it has been known that it can be made of either a binary system ceramics such as $\text{Pb}(\text{Ti}, \text{Zr})\text{O}_3$, ternary
 10 system ceramics such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_x\text{Ti}_y\text{Zr}_z\text{O}_3$, or a quadruple system ceramics such as $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_A(\text{Sn}_{1/3}\text{Nb}_{2/3})_B\text{Ti}_C\text{Zr}_D\text{O}_3$.

Almost all constituting elements of these ceramics have ceramics compositions, and these can be obtained by molding the raw ceramics materials or calcined powders of these into a desired form, and firing the mold at a high temperature. On the other hand, ferroelectric ceramics composites can be derived by
 15 mixing the powder of above cited ceramics into organic material such as rubber or epoxy resin, and can be produced through a relatively low temperature manufacturing process.

Since the conventional ferroelectric ceramics have to be fired at a relatively high temperature ranging from 1100 to 1300 °C, only refractory metal such as platinum can be employed as the internal electrodes of the ceramics elements such as a piezoelectric element and a pyroelectric element.

Moreover, since these ceramics can hardly be formed into films, only refractory metal such as platinum or heat-resistive ceramics can be used as the forming substrate thereof. On the other hand, since the ferroelectric ceramics composites comprised of ferroelectric ceramics and organic material are definitely disadvantageous in terms of their low heat-resistance and low mechanical Q factors, these can hardly be
 20 used as the ceramics elements of oscillators or filters.

Meanwhile, as for the electrostrictive ceramics which is a family of dielectric ceramics, the binary system ceramics such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_x\text{Ti}_y\text{O}_3$, and ternary system ceramics such as $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 - $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ had been known by the Japanese Patent Publication No. 61-31926.

Almost all the constituting elements of these ceramics are of ceramic compositions also, and these ceramics can be obtained by molding the raw ceramics materials or calcined powders of these into a
 30 desired form, and firing the mold at a high temperature. Meanwhile, electrostrictive ceramics composites can be derived by mixing the powder of above cited ceramics into an organic material such as rubber or epoxy resin, and can be produced through a relatively low temperature manufacturing process.

Since actuator elements utilizing the electrostrictive ceramics require no polarizing process afterward, and show no hysteresis in electric field vs strain, less deterioration of characteristics by aging, and higher
 35 heat resistance over the one utilizing the conventional piezoelectric ceramics, the actuator elements made of these ceramics are now extensively employed in various actuators.

Since the firing temperature of conventional electrostrictive ceramics is relatively high, and it is within a range from 1100 to 1300 °C, only refractory platinum can be employed as the internal electrodes of these actuator elements.

In addition to the above, since these electrostrictive ceramics can hardly be formed into films, and the forming substrate can be constituted of only refractory platinum or highly heat resistive ceramics. On the other hand, since the electrostrictive ceramics composites comprised of electrostrictive ceramics and organic material are definitely disadvantageous because of their low heat resistance and low elastic constants, so that these can hardly withstand against high amplitude mechanical stresses.

A new ceramics composite material having high heat resistance and excellent dielectric properties, which can be produced through a relatively low temperature manufacturing process.

The ceramics composite material of the invention comprises a dielectric ceramics and a glass having a softening temperature lower than the sintering temperature of the dielectric ceramics. However, the dielectric ceramics mentioned in the present invention correspond to a ferroelectric ceramics and an
 50 electrostrictive ceramics.

The ferroelectric ceramics employed here can be a binary system ceramics such as $\text{Pb}(\text{Ti}, \text{Zr})\text{O}_3$, ternary system ceramics such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_x\text{Ti}_y\text{Zr}_z\text{O}_3$ (where $X+Y+Z=1$), a quadruple system ceramics such as $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_A(\text{Sn}_{1/3}\text{Nb}_{2/3})_B\text{Ti}_C\text{Zr}_D\text{O}_3$ (where $A+B+C+D=1$), or a ferroelectric ceramic composition such as BaTiO_3 , PbTiO_3 , PbNb_2O_6 , $(\text{Na}, \text{K})\text{NbO}_3$, etc.

The electrostrictive ceramics employed here can be a binary system ceramics such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_x\text{Ti}_y\text{O}_3$ (where $X+Y=1$), ternary system ceramics such as $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 - $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$, or other electrostrictive ceramics composition. Furthermore, the glass employed here can be a glass of either
 55 $\text{PbO} \cdot \text{B}_2\text{O}_3$, $\text{PbO} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$, $\text{PbO} \cdot \text{ZnO} \cdot \text{B}_2\text{O}_3$, $\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$, or other system.

The ceramics composite material of the present invention can be prepared by mixing the powder of dielectric ceramics and the powder of glass having a softening temperature lower than the sintering temperature of the dielectric ceramics, and by firing the mixture of these two.

Since it can be fired at a temperature close to the softening temperature of the glass powder (e.g., in a range from 300 to 800 °C), the ceramics composite material can be prepared at a temperature considerably lower than the sintering temperature of conventional ceramics comprised of purely dielectric ceramics, and this fact is advantageous from the aspect of manufacturing various ceramic elements.

For an instance, stainless steel or such which is less heat resistive can be used as a substrate forming the ceramics composite materials of the invention.

Comparing with the conventional ceramics composite materials prepared by mixing the powder of dielectric ceramics into organic resin, the ceramics composite material of the invention is superior than the former in respect of the heat resistance because no organic material which are subject to thermal deterioration is included therein.

Therefore, the ceramics composite material of the invention can be extensively utilized to construct various piezoelectric, pyroelectric, ferroelectric memory, and actuator elements. Since its relatively low firing temperature is particularly advantageous to construct ceramics elements by coating the ceramics composite on a substrate and by firing this afterward.

Moreover, since the ceramics composite material of the invention can be produced by using very fine dielectric ceramics powder and glass powder having very small average particle sizes, the elements can be made into a form of very thin film.

Fig. 1 is a schematic sectional view of the invented ceramics composite material comprising a dielectric ceramics and a glass, and this shows its structure.

Fig. 2 is a schematic sectional view of the piezoelectric, pyroelectric, or ferroelectric element made of the invented ceramics composite material comprising a ferroelectric ceramics and a glass. This shows its fundamental structure.

Fig. 3 is a schematic sectional view of the actuator element made of the invented ceramics composite material comprising an electrostrictive ceramics and a glass. This shows its fundamental structure.

Now a ferroelectric ceramics composite material consisted of a ferroelectric ceramics and a glass, which is one of the preferred modes of the invention, is explained in the followings for its detail. As shown in Fig. 1, the ferroelectric ceramics composite material 1 consists of particles of ferroelectric ceramics 2 which are randomly dispersed into a matrix of glass 3.

The ceramics composite material 1 having the abovesown structure can be prepared by mixing powders of ferroelectric ceramics and glass having a softening temperature lower than the sintering temperature of said ceramics, and by firing the mixture at a temperature lower than the sintering temperature of the ceramics and equal or higher than the softening temperature of the glass.

Since only the glass powder melts and no change of the ceramics particles is produced at that temperature range, the particles of ferroelectric ceramics 2 are evenly dispersed and fixed in the matrix of glass 3.

The average particle size of the ferroelectric ceramics 2 in this case is desirable to 2 microns (micron meters) or smaller in order to attain a high packing density of the ceramics composite material 1. When the ceramics powder having an average particle size of 0.6 microns or smaller is employed, the ceramics composite material 1 having an extremely high packing density of 98% or more to the theoretically attainable density can be obtained.

In contrast to the above, when ceramics powder having an average particle size more than 2 microns is employed, ceramics composite material 1 having a lower packing density, or porous composite material, is produced. Satisfactory results will be obtained when ferroelectric ceramics powder having an average particle size exceeding the critical particle size of the ferroelectricity is employed.

The volume proportion between the ferroelectric ceramics and the glass is arbitrary determined according to the desired ferroelectric characteristics. However, an excessively high volume of the ferroelectric ceramics may result in inadequate sintering because of the lower firing temperature. On the other hand, an excessively small volume of it may result in inadequate electrical characteristics. Therefore, the volume proportion of the ferroelectric ceramics in the ceramics composite material is desirable to set within a range from 10 to 90%.

As for the ferroelectric ceramics 2 mentioned in the invention, any of the ferroelectric ceramics can be employed. More concretely, any of the binary system ceramics having a composition such as $\text{Pb}(\text{Ti}, \text{Zr})\text{O}_3$, ternary system ceramics composition such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_x\text{Ti}_y\text{Zr}_z\text{O}_3$ (where $x + y + z = 1$), the quadruple system ceramics composition such as $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_A(\text{Sn}_{1/3}\text{Nb}_{2/3})_B\text{Ti}_C\text{Zr}_D\text{O}_3$ (where $A + B + C + D = 1$), or the ferroelectric ceramics composites containing BaTiO_3 , PbTiO_3 , PbNb_2O_6 , $(\text{Na}, \text{K})\text{NbO}_3$, etc. can be em-

ployed.

As for the glass 3 mentioned in the invention, any of the glass materials having a softening temperature lower than the sintering temperature of the ferroelectric ceramics can be employed. More concretely, the employment of any of the glasses such as $\text{PbO} \cdot \text{B}_2\text{O}_3$, $\text{PbO} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$, $\text{PbO} \cdot \text{ZnO} \cdot \text{SiO}_2$, $\text{ZnO} \cdot \text{B}_2\text{O}_3 \cdot \text{SiO}_2$, or other system, is desirable.

Furthermore, the employment of a crystallized glass derived from the above-mentioned glass is highly desirable because of its possible higher heat resistance of the obtained ceramics composite material. The employment of a glass having a high chemical stability and a thermal expansion coefficient close to that of the ferroelectric ceramics is also highly desirable.

In the present invention an electrostrictive ceramics composite material can be derived by employing an electrostrictive ceramics instead of the above-described ferroelectric ceramics.

The electrostrictive ceramics mentioned here can be a binary system ceramics such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ (where $x+y=1$), ternary system ceramics such as $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 - $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$, or other electrostrictive ceramics compositions.

The desirable average particle size and the volume proportion of the electrostrictive ceramics in this case are identical with those of the case of ferroelectric ceramics composites. That is, the average particle size of the electrostrictive ceramics is desirable to 2 microns or smaller and preferably 0.6 microns or smaller for attaining a dense packing density thereof.

In contrast to the above, the lower limit of average particle size is determined by critical particle size of electrostriction. The desirable volume proportion in this case is within a range from 10 to 90% also.

Although the above explanation has been made for the ceramics composite material consisted of ferroelectric ceramics (or electrostrictive ceramics) and glass, the ceramics composite material of the invention can be obtained by employing these constituting ceramics and glass as the main materials, and other ceramics materials such as alumina, zirconia, titania, or others can be added thereto so far as these materials do not obstruct the purpose of the invention.

Then, a ceramics composite material comprised of the abovedescribed dielectric ceramics (ferroelectric ceramics or electrostrictive ceramics), glass and inorganic whiskers is then explained below.

The objective of the addition of inorganic whiskers is to improve the mechanical strength such as the flexural strength, and a proper amount of the whiskers of magnesia, zirconia, SiC , Si_3N_4 , ZnO , potassium titanate, barium titanate, strontium titanate, or other ceramics can be employed. Besides, the fiber of glass such as heat-resistive silica glass can be employed as the whiskers.

The size of the employed whiskers is preferably within a range from 2 to 50 microns. The whiskers having a fiber length more than 50 microns may tend to lower the packing density, and ferroelectric or electrostrictive properties, the whiskers having a length less than 2 microns may contribute very little to improve the flexural strength of the composite. Beside the above, the employment of whiskers having a length proportionally shorter to the average particle size of dielectric ceramics is recommendable.

The amount of whisker addition is desirable to 15 volume% or less for the dielectric ceramics composite, otherwise, the ferroelectric or electrostrictive properties will be sacrificed.

Several examples of the invention are now shown in the followings.

Example 1

In preparing a first example of the invention, a ferroelectric calcined powder material of $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.99}(\text{Sn}_{1/3}\text{Nb}_{2/3})_{0.09}\text{Ti}_{0.42}\text{Zr}_{0.40}\text{O}_3$ ceramics added by 0.5 wt% of MnO_2 , which was prepared by mixing its raw powder materials, calcining the mixture at 1250°C for two hours and pulverizing down into particles having an average size of about 4 microns by means of a ball-mill, was mixed with the powder of $\text{PbO} \cdot \text{B}_2\text{O}_3$ system CF-8 glass having an average particle size of 3.8 microns and including a small amount of ceramics, manufactured by Nippon Electric Glass Co., Ltd., at a volume ratio shown in Table 1.

After ethanol as a dispersive medium was added to the mixture of these powders, the mixture was pulverized down to a powder having an average particle size of about 0.2 microns by using a media agitating mill (Motor Mill M50, manufactured by Eiger Engineering, Ltd., wherein zirconia balls having an average diameter of 0.4 mm were used and the mill was driven at a rim speed of 10 m/s), and the mixture was dried afterward.

The product was then granulated by using pure water, and the granules were sized by using a 500 micron filter.

Then, thus obtained granules were pressed into a die to form a disk having a diameter of 13 mm and thickness of about 1 mm. The ferroelectric ceramics composite samples specified by Nos. 2 to 7 were obtained by firing the disk in an electric furnace at the firing temperature shown in Table 1 for two hours.

Both the temperature increment and decrement rates employed thereat were 400 °C per hour.

Then, Cr-Au double layered electrodes were deposited on both sides of the fired disk, and the piezoelectric elements having a structure shown in Fig. 2 were prepared by applying a DC electric field of 3 kV/mm: thereon in a silicon oil bath kept at 100 °C for 30 minutes for polarization. In Fig. 2, 1 is a ferroelectric ceramics composite, and 4 is a pair of electrodes.

The dielectric constants, electromechanical coupling coefficients, dielectric loss-tangents of these sample disks were determined, and the results of these are tabulated in Table 1. However, No. 1 and No. 8 sample refer to the ceramics samples prepared for the purpose of contrasts only, so that the data of these should be excluded.

Table 1

No.	Mixing Ratio (in Vol.%)		Firing temp. (°C)	Coupling coefficient Kp	Dielectric const. at 1 kHz	Dielectric loss-tang. at 1 kHz
	Ferro. powder	Glass powder				
1	0	100	430	0	43	0.0087
2	10	90	400	0.05	75	0.0084
3	20	80	450	0.15	176	0.0049
4	40	60	450	0.19	210	0.0041
5	60	40	500	0.29	312	0.0048
6	80	20	500	0.31	329	0.0052
7	90	10	550	0.30	283	0.0083
8	100	0	1150	0.55	1260	0.0051

Wherein Ferro.means Ferroelectric ceramics.

As seen in Table 1, although the coupling coefficients and dielectric constants of the ferroelectric ceramics composite samples specified by Nos. 2 to 7 are slightly lower than those of No. 8 contrast sample, these can be prepared at firing temperatures considerably lower than that for the contrast. Moreover, if the No. 8 contrast sample is fired at a temperature lower than 1000 °C, it will not be sintered and show zero coupling coefficient, i.e., no piezoelectricity.

The average particle size of the ferroelectric ceramics particles in samples Nos. 2 to 7 determined by microscopic observation is about 0.2 microns, and this is identical with that of the unfired samples.

An experiment same as the above was conducted for the cases where the average particle sizes of the ferroelectric ceramics powder pulverized by using the media agitating mill were different from those of afore-mentioned samples, and the ferroelectric ceramics powder and the glass powder were mixed at a ratio same as the one employed to prepare No. 5 sample. The densities of the fired samples made of the pulverized and mixed powder having average particle sizes of 1.9, 0.92, 0.58, 0.22 and 0.052 microns were 92, 94, 98, 98, and 98% of the respective theoretical densities.

Thus, densities of more than 90% of the theoretical densities were obtained when powders having average particle sizes of 2 microns or smaller were employed. Particularly when a powder having an average particle size of 0.6 microns or smaller was employed, a ceramics composite having an extremely high density of 98% was obtained.

In the above-explained embodiments, a method to prepare the ceramics composites from the mixed powder of ferroelectric ceramics and glass which was pulverized together, were shown. However, the identical results are obtained by mixing the powder of ferroelectric ceramics and the powder of glass which are independently pulverized.

When this manufacturing method was employed, the respective densities of the fired ceramics composites obtained by using powders having average particle sizes of 4.2, 1.8 and 0.45 microns were 69, 88, and 94% respectively to the theoretical densities. In this case, high density ceramics composites are obtained also when powder having an average particle size of 2 microns or smaller is employed.

The critical particle size showing the ferroelectricity was found to be approximately 0.02 microns in the cases of ferroelectric ceramics composites of the present example, so that the ferroelectric ceramics composites can be obtained when a ferroelectric ceramics powder having an average particle size of about 0.02 microns or more is employed.

The displacement of the piezoelectric elements in the thickness direction was determined by using a differential transformer type displacement meter when a DC electric field of 2 kV/mm was applied between the electrodes of the polarized No. 5 specimen. A displacement of 0.38 microns in the thickness direction was observed so that a function as a mechanical actuator was confirmed.

- 5 Furthermore, the terminal voltage generated between the electrodes when a temperature change was given to the No. 5 sample, was measured. Since this experiment confirmed a generation of voltage proportional to the magnitude of the temperature change, a function as a pyroelectric element of this element was confirmed.

- 10 The D-E hysteresis loop of the No. 5 ceramics composite was also measured, and the results showed an coercive force E_c of 2.3 kV/mm and a residual polarization P_r of 14.6 $\mu\text{C}/\text{cm}^2$ so that a function of the ceramics composite as a ferroelectric memory element was confirmed.

Example 2

- 15 In preparing Example 2 of the invention, a ferroelectric calcined powder material of $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{0.09}(\text{Sn}_{1/3}\text{Nb}_{2/3})_{0.09}\text{Ti}_{0.42}\text{Zr}_{0.40}\text{O}_3$ ceramics added by 0.5 wt% of MnO_2 , which was prepared by mixing its raw powder materials, calcining the mixture at 1250°C for two hours and pulverizing down into particles having an average size of about 4 microns by means of a ball-mill, was mixed with the glass powder employed to prepare Example 1 at the ratios shown in Table 2.

- 20 After ethanol as a dispersive medium was added to the mixture of these powders, the mixture was pulverized down to a powder having an average particle size of about 0.2 microns by using a media agitating mill same as the one used in Example 1, and the mixture was dried afterward.

- Then, magnesia whiskers having an average diameter of about 2 microns and an average length of 24 microns were shown in Table 2, and the mixture was made into granules by using pure water, and the granules were sized by passing through a 500 micron mesh filter. The granules were pressed into a die to form a disk having a diameter of 13 mm and a thickness of about 1 mm. The ferroelectric ceramics composite samples specified by Nos. 9 to 11 were obtained by firing the disks in an electric furnace at the firing temperature shown in Table 2 for two hours. Both the temperature increment and decrement rates employed thereat were 400°C per hour.

- 30 Then, Cr-Au electrodes were deposited on both sides of the fired disk, and the ferroelectric ceramic disks were prepared by applying a DC electric field of 3 kV/mm thereon in a silicon oil bath kept at 100°C for 30 minutes for polarization.

- The dielectric constants, electromechanical coupling coefficients, dielectric loss-tangents and flexural strengths of these sample disks were measured, and the results of these are tabulated in Table 2. However, sample No. 9 refers to a ceramics sample containing no whiskers, and this is used as a contrast only.

Table 2

40

No.	Mixing Ratio (in Vol.%)			Firing temp. (°C)	Flexural strength (MPa)	Coupling coef. Kp	Dielectric const. at 1 kHz	Dielectric loss-tang. at 1 kHz
	F	G	W					
45 9	50	50	0	450	81	0.29	312	0.0045
10	50	45	5	450	95	0.30	305	0.0039
11	50	40	10	450	102	0.28	301	0.0042

50 F: powder of ferroelectric ceramics, G: Glass powder, W: magnesia whiskers.

As shown in Table 2, the flexural strengths of the ferroelectric ceramics composite samples containing whiskers specified by Nos. 10 and 11 are higher than the one without containing the whiskers.

Example 3

55 Two sample Nos. 12 and 13 of the invention were prepared by using the materials employed to prepare the sample No. 3 in Example 1 and the sample No. 10 in Example 2, except that a crystallized glass ($\text{PbO} \cdot \text{ZnO} \cdot \text{B}_2\text{O}_3$ system glass LS-7105, having an average particle size of 7.5 microns and a softening

temperature of 400°C, manufactured by Nippon Electric Glass Co., Ltd) was employed in this case. The ferroelectric ceramics composite samples were manufactured by the method employed in Examples 1 and 2.

The electrical characteristics such as the dielectric constants and the deformation temperature of these samples were measured, and the results of these are tabulated in Table 3 together with the ones of sample Nos. 3 and 10. However, the deformation temperature is defined as the temperature at which the edge of disk sample is rounded off after it is kept for a period of 5 hours.

Table 3

No.	Type of glass	Firing temp. (°C)	Coupl. coef. Kp	Dielectric constant at 1 kHz	Dielectric loss-tang at 1 kHz	Deformation temp. (°C)
3	Amorphous glass	450	0.15	176	0.0049	560
12	Crystallized glass	450	0.16	201	0.0067	700 or higher
10	Amorphous glass	450	0.30	305	0.0039	560
13	Crystallized glass	450	0.32	330	0.0051	700 or higher

As shown in Table 3, the deformation temperature of ferroelectric ceramics composites can be substantially higher by using a crystallized glass over the case where amorphous glass is employed. This means a substantially higher heat resistance of the ferroelectric ceramics composite which can withstand against mechanical machining conducted at a high temperature or high-temperature heat-treatment.

Example 4

In preparing Example 4 of the invention, a calcined powder of $0.5\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.4PbTiO_3 - $0.1\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ electrostrictive ceramics was prepared by calcining a mixture of its raw materials at 1200°C for two hours, and it was pulverized into particles having an average size of about 3.2 microns by means of a ball-mill. Then, it was mixed with the glass powder employed to prepare samples of Example 1 at the ratios shown in Table 4.

After ethanol as a dispersive medium was added to the mixture of these powders, the mixture was pulverized down to a powder having an average particle size of about 0.2 microns by using a media agitating mill same as the one used in Example 1, and the mixture was dried afterward.

Then, the mixture was made into granules by using pure water, and the granules were sized by using a 500 micron mesh filter. The granules were then pressed into a die to form a rectangular plate having a length of 10 mm, a width of 5 mm and a thickness of about 1 mm. The samples of electrostrictive ceramics composite specified by Nos. 15 to 20 shown below were obtained by firing the plates in an electric furnace at the firing temperature shown in Table 4 for two hours. Both the temperature increment and decrement rates employed thereat were 400°C per hour.

Then, Cr-Au double-layered electrodes were deposited on both sides of the fired disk, and the electrostrictive ceramic disks were prepared by applying a DC electric field of 2 kV/mm thereon for polarization.

The displacements along the lengthwise direction were measured by using a differential transformer type displacement meter, and the results are tabulated in Table 4 wherein the displacement in % is expressed by a displacement ratio against the sample length before the electric field is applied, and the samples Nos. 14 and 21 are contrasts, and the data thereof should be excluded.

Table 4

No.	Mixing Ratio (in Vol.%) Powder of ferro-electric ceramics	Powder of glass	Firing temp. (*C)	Displacement (%)
14	0	100	430	0.0
15	10	90	400	0.002
16	20	80	450	0.009
17	40	60	450	0.011
18	60	40	500	0.017
19	80	20	500	0.020
20	90	10	550	0.018
21	100	0	1120	0.035

As seen from Table 4, the displacements of the electrostrictive ceramics composite samples Nos. 15 to 20 are slightly lower than that of the contrast sample No. 21, but these can be fired at temperatures substantially lower than that of the contrast. Moreover, if the contrast sample No. 21 is fired at a temperature less than 1000 °C, it is not sintered.

The average particle size of the electrostrictive ceramics particles in samples Nos. 15 to 20 determined by microscopic observation is about 0.2 microns, and this is identical with that of the unfired samples.

An experiment same as the above was conducted for the cases where the average particle sizes of the electrostrictive ceramics powder pulverized by using the media agitating mill were different from those of the afore-mentioned samples, and the electrostrictive ceramics powder and the glass powder were mixed at a ratio same as the one employed to prepare No. 18 sample. The densities of the fired samples made of the pulverized and mixed powder having average particle sizes of 2.4, 1.12, 0.56, 0.19 and 0.063 microns were 93, 94, 98, 99 and 98% of the respective theoretical densities.

Thus, densities of more than 90% of the theoretical densities are obtained when powders having average particle sizes of 2.4 microns or smaller were employed. Particularly when a powder having an average particle size of 0.6 microns or smaller was employed, a ceramics composite having an extremely high density of 98% or more was obtained.

In the above-explained Example 4, a method to prepare the ceramics composites from the mixed powder of electrostrictive ceramics and glass which was pulverized together, were shown. However, the identical results are obtained by mixing the powder of electrostrictive ceramics and the powder of glass which are independently pulverized.

When this manufacturing method was employed, the respective densities of the fired ceramics composites obtained by using powders having average particle sizes of 3.2, 1.9 and 0.51 microns were 70, 89 and 93% respectively to the theoretical densities. In this case, high density ceramics composites are obtained also when powder having an average particle size of 2 microns or smaller is employed.

In the above-explained Example 4, the critical particle size showing electrostrictivity in the electrostrictive ceramics composites was found to be about 0.02 microns, so that an electrostrictive ceramics composite can be obtained when electrostrictive ceramics particles having an average particle size of 0.02 microns or more is employed.

Example 5

In preparing Example 5 of the invention, a calcined powder of $0.5\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.4PbTiO_3 - $0.1\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ electrostrictive ceramics which was prepared by mixing its raw materials, calcining the mixture at 1200 °C for two hours and pulverizing into particles having an average size of about 3.2 microns by means of a ball-mill, was mixed with the glass powder employed to prepare samples of Example 1 at the ratios shown in Table 5.

After ethanol as a dispersive medium was added to the mixture of these powders, the mixture was pulverized down to a powder having an average particle size of about 0.2 microns by using a media agitating mill same as the one used in Example 1, and the mixture was dried afterward.

Then, magnesia whiskers having an average diameter of about 2 microns and an average length of about 24 microns were added to the dried mixture, and the mixture was made into granules by using pure water, and the granules were sized by using a 500 micron mesh filter. The granules were then pressed into a die to form a rectangular plate having a length of 10 mm, a width of 5 mm and a thickness of about 1 mm. The samples of electrostrictive ceramics composite specified by Nos. 23 and 24 shown below were

obtained by firing the plates in an electric furnace at the firing temperature shown in Table 5 for two hours. Both the employed temperature increment and decrement rates were 400 °C per hour.

Then, Cr-Au double-layered electrodes were deposited on both sides of the fired disk, and the electrostrictive ceramic disks were prepared by applying a DC electric field of 2 kV/mm thereon for polarization.

The displacements along the lengthwise direction were measured by using the previously mentioned differential transformer type displacement meter and the flexural strengths were measured. The results of these are tabulated in Table 5 wherein the sample No. 22 is a contrast in which no whiskers are included.

Table 5

No.	Mixing Ratio (in Vol.%) Powder of electro-strictive ceramics	Powder of glass	Magnesia whiskers	Firing temp. (°C)	Flexural Strength (MPa)	Displacement (%)
22	50	50	0	450	63	0.018
23	50	45	5	450	88	0.017
24	50	40	10	450	101	0.016

Table 5 shows that the flexural strengths of Nos. 23 and 24 electrostrictive ceramics composite samples containing whiskers are considerably higher than that of the contrast sample No. 22 containing no whiskers.

Example 6

Two samples Nos. 25 and 26 of the invention were prepared by using the materials employed to prepare No. 16 sample in Example 4 and No. 23 sample in Example 5, except that a crystallized glass (PbO·ZnO·B₂O₃ system glass LS-7105, having an average particle size of 7.5 microns and a softening temperature of 400 °C, manufactured by Nippon Electric Glass Co., Ltd.) was employed in this case.

The electrostrictive ceramics composite samples were manufactured by the method substantially identical with the one employed in Example 4 and 5.

The displacements and the deformation temperatures of these samples were measured, and the results of these are shown in Table 6 together with the ones of Nos. 16 and 23. However, the deformation temperature is defined as the temperature at which the edge of disk sample is rounded off after it is kept for a period of 5 hours.

Table 6

No.	Type of glass	Firing temp. (°C)	Displacement (%)	Deformation temperature(°C)
16	Amorphous glass	450	0.009	560
25	Crystallized glass	450	0.010	700 or higher
23	Amorphous glass	450	0.017	560
26	Crystallized glass	450	0.020	700 or higher

As shown in Table 6, the deformation temperatures of electrostrictive ceramics composites comprised of crystallized glass are substantially higher than the samples comprised of amorphous glass. This means a substantially higher heat resistance of the electrostrictive ceramics composite which can withstand against mechanical machining conducted at a high temperature or high-temperature heat-treatment.

Example 7

In preparing Example 7 of the invention, a calcined powder of 0.5Pb(Ni_{1/3}Nb_{2/3})O₃-0.4PbTiO₃-0.1Ba-(Zn_{1/3}Nb_{2/3})O₃ electrostrictive ceramics which was prepared by mixing its raw materials, calcining the mixture at 1200 °C for 10 hours and pulverizing into particles having an average size of about 3.2 microns by means of a ball-mill, was mixed with the glass powder employed to prepare samples of Example 1 at a ratio employed to prepare No. 17 sample in Table 4.

After ethanol as a dispersive medium was added to the mixture of these powders, the mixture was pulverized down to a powder having an average particle size of about 0.2 microns by using a media agitating mill same as the one used in Example 1, and this slurry was dip-coated on the both sides of a stainless-steel plate having a length of 20 mm, a width of 5 mm, and a thickness of 0.05 mm leaving a 5 mm-long space on the end of plate.

The coated electrostrictive ceramics composite layer was dried and fired at a temperature of 450 °C for two hours. Cr-Au double layered electrodes were deposited on both sides of the thus-obtained electrostrictive ceramic thinfilm having an average thickness of 0.045 mm, saving 1 mm wide strip regions on the peripheral regions on both sides. And then, thus-obtained electrostrictive element was mounted into an actuator element.

A schematic sectional view of the actuator element is shown in Fig. 3 wherein the numeral 10 is an electrostrictive ceramics composite film formed on the stainless steel plate 12, 11a and 11b are the Cr-Au electrodes formed on the electrostrictive ceramics composite film 10, and 13 is a mounting block on which an end 14 of the electrostrictive element is mounted. The electrostrictive element is mounted on the mounting block 13 by means of an epoxy-resin adhesive.

An application of DC potential between the electrode 11a or 11b and the stainless steel plate 12 will cause a displacement of the free-end 15 of the element in right or left direction while the mounted end 14 is fixed.

The flexure displacement of the free-end 15 of the element produced by an application of 2 kV/mm electric field between the electrode 11a and the stainless steel plate, was measured by means of an optical microscope, and a leftward displacement of the free-end of 122 microns was confirmed. Likewise, a rightward displacement of 105 mm was observed when the same electric field was applied between the electrode 11b and the stainless steel plate 12.

25 Claims

1. A dielectric ceramics composite material comprising:
a dielectric ceramics and
a glass having a softening temperature lower than the sintering temperature of said dielectric ceramics.
2. A dielectric ceramics composite material according to claim 1, to which inorganic whiskers are dispersed as an additional constituting element.
3. A dielectric ceramics composite material according to claim 1 or 2, wherein the average particle size of said dielectric ceramics is 0.6 micron meters or less.

FIG. 1

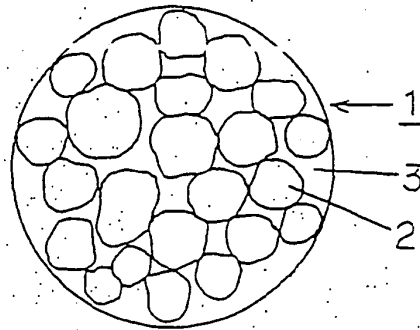


FIG. 2

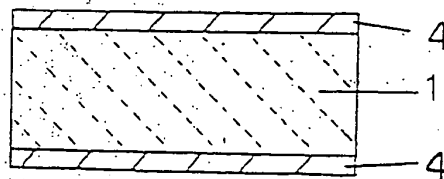
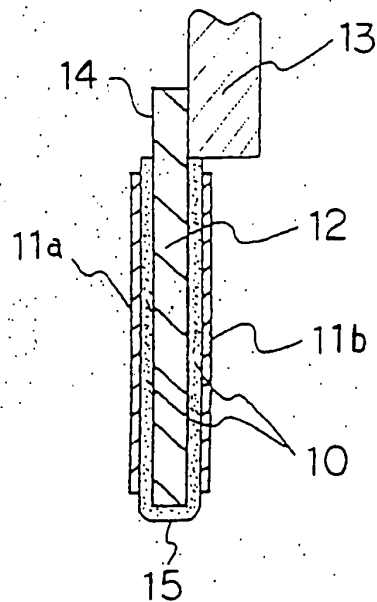


FIG. 3



DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	GB-A-2 161 647 (THE GENERAL ELECTRIC COMPANY PLC) * the whole document *	1-3	H01L41/18
X	PATENT ABSTRACTS OF JAPAN vol. 14, no. 479 (E-992)18 October 1990 & JP-A-21 97 181 (MURATA MFG CO LTD) 3 August 1990 * abstract *	1	
X	PATENT ABSTRACTS OF JAPAN vol. 8, no. 49 (E-230)6 March 1984 & JP-A-58 204 579 (KINSEKI KK) 29 November 1983 * abstract *	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			H01L
The present search report has been drawn up for all claims			
Place of search THE HAGUE	Date of completion of the search 02 FEBRUARY 1993	Examiner PELSERS L.	
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